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(54) Title: PROCESS FOR THE PREPARATION OF VANADYL SULFATE SOLUTION

(57) Abstract: A process for producing a vanadyl sulphate solution (VOSO₄) comprises forming a suspension of vanadium trioxide (V₂O₃) in a sulphuric acid solution and contacting the V₂O₃ suspension with a strong oxidising agent under controlled conditions to produce the VOSO₄ solution. A preferred oxidising agent is hydrogen peroxide, which is added very slowly to the V₂O₃ suspension due to the violent nature of the reaction.

- 1 -

PROCESS FOR THE PREPARATION OF VANADYL SULFATE SOLUTION

BACKGROUND TO THE INVENTION

THIS invention relates to a process for the preparation of a vanadyl sulphate solution.

It is known to produce vanadyl sulphate by dissolving vanadium pentoxide in hot dilute sulphuric acid under vigorous agitation and continued heating with the aid of sulphur dioxide as a reducing agent.

The limited solubility of sulphur dioxide in acidic and aqueous solutions results in the emission of sulphur dioxide from the solution and this presents an environmental hazard. Overdosing of the solution with SO₂ gas results in the unwanted formation of the lower valent vanadium sulphate, namely V₂SO₄ and not vanadyl sulphate (VOSO₄).

Since the dissolution of vanadium pentoxide in sulphuric acid is endothermic heat has to be provided to drive the formation of vanadyl sulphate.

There is thus always a need for a new method for the production of vanadyl sulphate.

- 2 -

SUMMARY OF THE INVENTION

According to the invention a process for producing a vanadyl sulphate solution includes the steps of:

- (1) providing a starting material comprising vanadium trioxide (V_2O_3);
- (2) contacting the vanadium trioxide with an appropriate volume and concentration of a sulphuric acid solution to produce a vanadium trioxide suspension; and
- (3) contacting the vanadium trioxide suspension with a strong oxidising agent that is capable of raising the valency or oxidation state of the vanadium, thereby to dissolve the vanadium trioxide in the sulphuric acid to produce the vanadyl sulphate solution ($VOSO_4$).

Various strong oxidising agents including peroxides and permanganate such as hydrogen peroxide, sodium peroxide and potassium permanganate, for example, can be used. Hydrogen peroxide is particularly preferred as it does not introduce any impurities into the final product.

The hydrogen peroxide is typically added slowly to the vanadium trioxide suspension due to the violent nature of the reaction.

BRIEF DESCRIPTION OF THE DRAWING

The invention will now be described in more detail, by way of example only, with reference to the accompanying drawings in which:

- 3 -

Figure 1 is a graph indicating the mass relationship between varying quality V_2O_3 expressed as V_2O_5 against constant 4.5g V_2O_5 portions in a 4.0 molar sulphuric acid solution; and

Figure 2 indicates the reduction potential in mVolt against the mass of the V_2O_3 used.

DESCRIPTION OF A PREFERRED EMBODIMENT

The crux of the invention is to use a strong oxidising agent to dissolve vanadium trioxide (V_2O_3), commonly referred to as Hivox, in a sulphuric acid solution to produce vanadyl sulphate ($VOSO_4$).

In carrying out the process, a strong oxidising agent such as a peroxide or permanganate, for example, is used to dissolve the V_2O_3 in a warm sulphuric acid solution with constant stirring. Although various strong oxidising agents such as hydrogen peroxide, sodium peroxide, potassium permanganate, iodine, potassium iodate, potassium bromate, bromine, ammonium persulfate, persulfates of sodium and potassium, cerium (IV) sulphate, and potassium dichromate, for example, can be used, hydrogen peroxide is preferred as it does not introduce any impurities into the final product.

As the quality of industrial grade Hivox ranges typically from 115 to 122 percent equivalent V_2O_5 , figure 1 can be used in order to determine an appropriate quantity of V_2O_3 for use in the process, depending on the quality of the starting material used. The required solution can be obtained by monitoring the reduction potential thereof in mVolt, as shown in figure 2, during the dissolution process. The start of production of vanadyl sulphate is illustrated at the point where the graph dips sharply.

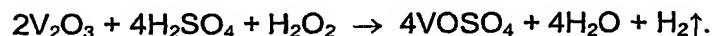
- 4 -

The invention will now be illustrated by way of the following non-limiting example.

Example

Hydrogen peroxide was used to dissolve 3.0 grams Hivox (V_2O_3) in a warm ($50^\circ C$) 4.0 molar sulphuric acid solution with constant stirring. The hydrogen peroxide was added dropwise as it reacted violently with the solution. During the dissolution process the reduction potential of the solution was continuously monitored and the addition of hydrogen peroxide stopped when the solution reached the end point at 600 mVolts.

The process proceeded according to the following formula:



During the process, the solution first turned green, which is indicative of the presence of V^{3+} ions, whereafter it turned blue, which is indicative of the presence of VO^{2+} ions present in the vanadyl sulphate end product.

From the above, it is evident that vanadyl sulphate can readily be made using Hivox (V_2O_3), which is generally more cost effective, and less hazardous, than the conventional process using V_2O_5 .

CLAIMS

1. A process for producing a vanadyl sulphate solution includes the steps of:
 - (1) providing a starting material comprising vanadium trioxide (V_2O_3);
 - (2) contacting the vanadium trioxide with a sulphuric acid solution to produce a vanadium trioxide suspension; and
 - (3) contacting the vanadium trioxide suspension with a strong oxidising agent that is capable of raising the valency or oxidation state of the vanadium, thereby to dissolve the vanadium trioxide in the sulphuric acid to produce the vanadyl sulphate solution ($VOSO_4$).
2. A process according to claim 1, wherein the strong oxidising agent is selected from the group comprising hydrogen peroxide, sodium peroxide, potassium permanganate, iodine, potassium iodate, potassium bromate, bromine, ammonium persulfate, persulfates of sodium and potassium, cerium (IV) sulphate, and potassium dichromate
3. A process according to claim 2, wherein the strong oxidising agent is hydrogen peroxide.
4. A process according to claim 3, wherein the hydrogen peroxide is added dropwise to the vanadium trioxide suspension.
5. A process according to claim 4, wherein the addition of hydrogen peroxide is stopped when the reduction potential of the vanadium sulphate solution reaches a predetermined end point.

- 6 -

6. A process according to claim 5, wherein the end point is at about 600mVolts.

1/1

Fig.1

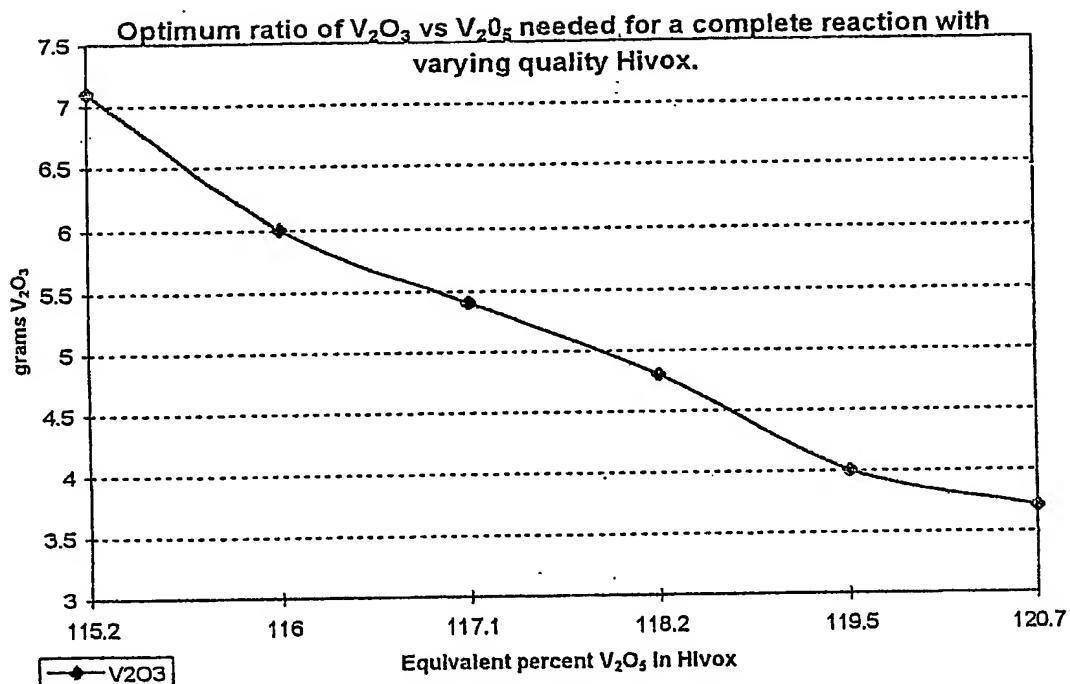
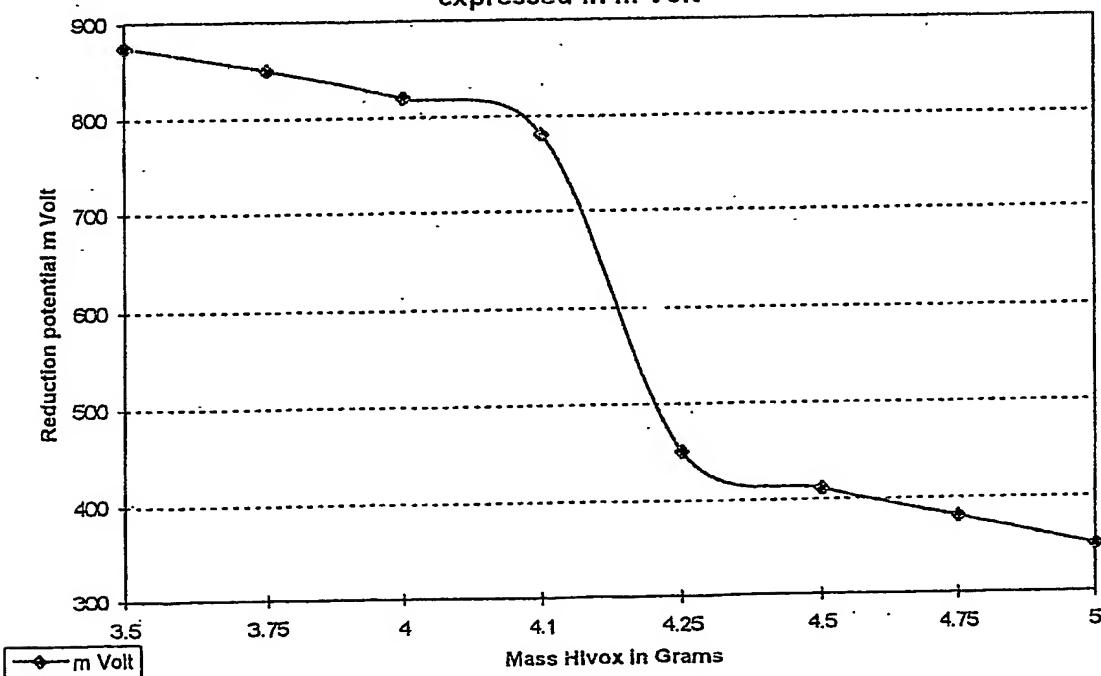


Fig.2

Optimum ratio of V_2O_3 vs V_2O_5 needed for a complete reaction expressed in m Volt



INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C01G31/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 02 04353 A (ROHRMANN BODO RUDIGER ; DORMEHL ANDRIES GERARDUS (ZA); HIGHVELD STE) 17 January 2002 (2002-01-17) the whole document	1-6
A	US 5 368 762 A (MAGOME KO ET AL) 29 November 1994 (1994-11-29) column 5, line 41 example 1	1-6

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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Patent document cited in search report	Publication date		Patent family member(s)	Publication date
WO 0204353	A 17-01-2002	AU WO ZA	6776901 A 0204353 A2 200105584 A	21-01-2002 17-01-2002 22-05-2002
US 5368762	A 29-11-1994	JP AU DE DE EP	5290871 A 641873 B1 69305905 D1 69305905 T2 0566019 A1	05-11-1993 30-09-1993 19-12-1996 10-04-1997 20-10-1993